

# Novel Tubing Microreactor for Monitoring Chemical Reactions

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There is an expanding interest in small-scale methods to evaluate catalysts and chemical reactions at a variety of conditions, ranging up to 6.9 MPa (1000 psig) and 300 °C. Multiwell parallel batch techniques are most commonly applied in high-throughput screening systems. In contrast, we describe here a rapid, serial, highly controllable method based on LC-type steel tubing rated for high pressures. The tube, containing a variety of flowing ingredients, such as carrier solvents, catalyst formulations, and reactants, is self-heated ohmically using electrical current from a power supply monitored and regulated with a precision of 0.01%. An array of voltage taps arranged along its length serves to sense the real-time temperature profile of the tube. Reactions are seen as temperature pulses progressing through the reactor, in zones of 200  $\mu$ L each, and tracked with a temperature precision of 0.1 °C. A unique pressure controller was devised to maintain constant reactor pressures despite effluent viscosity fluctuations due to polymerization. Several chemical reaction systems have been characterized to date, including decomposition reactions of di-*tert*-butyl peroxide, polymerizations of styrene, formation of polyethylene from ethylene, and copolymerization of ethylene with 1-octene. For ethylene polymerization, the amount of mass of polymer formed is proportional to the responses observed.

In the early 1990s, combinatorial methods were first reported for creating large numbers of candidate polypeptides in order to discover desirable ligand-binding properties.<sup>1</sup> Since then, parallel processing of large numbers of microamounts of different candidate substances has become a powerful approach for discovery over a wide range of applications, particularly in the field of pharmaceuticals. In the case of industrial catalysts, the reaction conditions for testing can be extreme by comparison, ranging beyond 300 °C and 3.4 MPa (500 psig). Programming the temperature of an array of samples held in thermostated blocks can also be relatively slow, particularly if elevated pressures are involved.

In 1988, it was shown that 1/16-in. LC tubing could be ohmically heated in alternating channels to create a pumping system with improved flow precision over conventional piston systems.<sup>2,3</sup> The key to its performance was 50 kilohertz pulse-

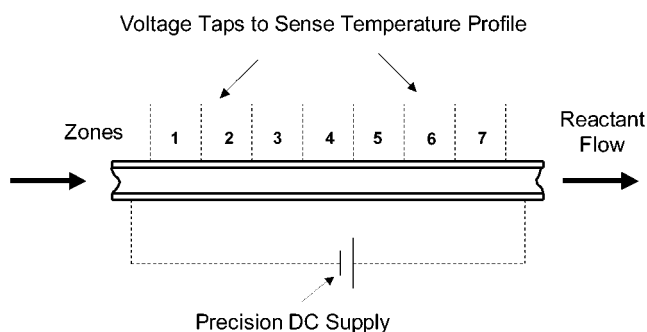


Figure 1. Resistance of the 1.59-mm o.d.  $\times$  1.27-mm i.d. (0.0625 in.  $\times$  0.050 in.) ss tubing wall is converted to temperature, as is done with thermal resistance devices (RTDs). By simultaneously monitoring voltages, the reaction front can be followed down the tube in 200- $\mu$ L zones.

width modulated control of electrical power applied directly to the tubing wall from special high-wattage toroidal transformers. The applied power was closely controlled in a dual PID loop configuration based on pressure and flow sensor information feedback. It was perceived at Dow that this heated tubing method could be adapted to the catalyst screening challenge, since the pressure, temperature, and residence times could be monitored and very rapidly changed within the tubing. Consequently, this article elaborates on our development of a tubing-based “electro-thermal microreactor” (ETMR).

Use of a programmable highly precise power supply affords control of the electrical current imparted to the entire reactor tube, equipped with voltage taps arrayed along its length. Since the relation between the tubing material’s resistivity and temperature are well-known, the control system computes the temperature of each zone from its respective voltage drop. In a sense, then, the reactor is composed of a series of hollow annular RTD (resistance temperature detectors) temperature sensors. The operating scheme is shown in Figure 1. The tubing simultaneously performs three distinct functions: as conduit for the various reaction substances, as heater, and as a linear series of temperature sensors.

Recently, high-temperature liquid chromatography has been investigated<sup>4,5</sup> showing excellent separation efficiencies and speed for certain compounds. The authors cite the importance of overcoming temperature gradients, in both axial and radial directions. From a thermal point of view, the ETMR system

(1) Lam, K. S., et al. *Letter to Nature*, **1991**, 354, 82–84.

(2) Miller, T. E., Jr.; Davis, C. M. *Anal. Chem.* **1988**, 60, 1965–1968.

(3) U.S. Patents 4,917,575 and 5,249,929.

(4) Yan, B., et al. *Anal. Chem.* **2000**, 72, 1253–1262.

(5) Thompson, J. D., et al. *Anal. Chem.* **2001**, 73, 3340–3347.

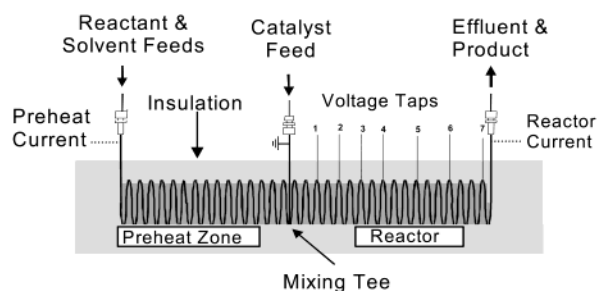


Figure 2. Tubing microreactor arrangement showing liquid feeds, electrical connections, and surrounding thermal insulation. The seven voltage tap wires are silver-soldered to the tubing to minimize contact resistance. The total volumes of the preheat zone and reactor are 1.6 and 1.8 mL, respectively.

reported here differs from this work with regard to the following: (1) Rather than a reservoir, such as an oil bath, as source of heat, in the case of the ETMR, the tubing wall itself generates all the heat to warm the eluent. This creates the unusual situation, other than when heat-generating reactions are occurring, that the inner and outer tubing surfaces are cooler than the center of the wall. (2) Rather than infer wall temperatures from heat transfer models, the ETMR actually measures average wall temperatures zone by zone along the tubing. In addition, (3) upon injection of catalysts into the flowing reactant, sizable heat pulses are generated chemically within the eluent itself.

## EXPERIMENTAL SECTION

**Reagents.** Anhydrous toluene (Sigma-Aldrich, Milwaukee, WI, part 24451-1, Pure-Pak) was purified by a method<sup>6</sup> developed at Dow to remove trace quantities of water, oxygen, and other impurities that deactivate the polymerization catalyst. Ethylene (BOC Gases, Murray Hill, NJ, 99.8% v/v purity) was scrubbed through a prepared<sup>6</sup> column containing both activated alumina and Q-5 reactant (supported copper redox catalyst).

**Apparatus.** The configuration of the reactor preheater, catalyst addition tee, and reactor itself are shown in Figure 2. Temperature tap wire leads were silver-soldered in place to minimize contact resistance. In the soldered mixing tee near the center, the side-stream addition tube was positioned so that its opening was centered in the flow stream.

The 1/16-in. (1.59 mm) o.d. reactor tubing inner diameter is generally 0.050 in. (1.27 mm), with a wall thickness of 0.00625 in. (0.16 mm). This 300-series HPLC grade stainless steel tubing (Alltech Associates, Inc., Deerfield, IL, part 30041) is rated for 70 MPa (10 000 psi) maximum working pressure.<sup>7</sup> Taken together with the tube length, generally ~150 cm, this thin wall is important to achieve resistances sufficiently high to allow self-heating at applied voltages available from high-precision, controllable power supplies. On the other hand, the wall is sufficiently thick to afford safe operation at these elevated pressures.

In various phases of development, the ETMR was configured for different flow systems. The most complex involves ethylene polymerizations, requiring that the entire unit be situated in an

oxygen-free drybox environment. This apparatus is shown in Figure 3. The control interface was designed using TestPoint (Capital Equipment Corp, Billerica, MA, version 4.0), a high-level control-oriented software package operating on the IBM PC platform. This is able to display the reaction zone pulses in real time while performing the many control tasks at a lower level.

As shown in Figure 3, toluene was generally used as a carrier solvent to convey reactants and catalysts through the ETMR. Toluene and other liquid feeds, such as comonomers, were delivered using a quaternary LC pump (Perkin-Elmer Corp., Norwalk, CT, part Series 200). Ethylene (a gas at STP) was metered through a mass flow controller (Porter Instrument Co., Inc., Hatfield, PA, part 201-DKBSVBAA) that had been modified to allow the flow chamber to be warmed to 60 °C, well above the critical temperature for ethylene. This arrangement results in a stream of ethylene to the reactor that is subsequently dissolved in the 1.90 mL/min toluene stream leading to the mixing tee. Catalyst additions were made using HPLC-type sample injection valves (6-port Valco valves supplied with auto injector described below). Separate precision pumps (Micro-Tech Scientific, Inc., Syunnyvale, CA, part UP200M) were used to supply toluene streams at typically 0.050 mL/min to these injection valves. An auto injector (LEAP Technologies, Carrboro, NC, part HTC-PAL) was used to sample and load various combinations of precatalysts and their associated activators. Given these parameters and the flow scheme shown in Figure 3, catalyst solutions are seen to be diluted about 20-fold within the microreactor. The PEEK tubing splices (Alltech Associates, Inc., part 32141) are necessary to isolate the voltages that power the self-heated reactor.

Details of the preheater and segmented temperature zone reactor are shown in Figure 2. The preheat segment is used to ensure temperature equilibration prior to addition of catalyst to ethylene monomer in the reactor zone. Independent adjustments of preheat and reactor temperatures make it possible to control the temperature along the length of the reactor.

**Electronics.** Control functions and measurements are made with a computer running TestPoint data acquisition software. The computer communicates with the reactor system through three interfaces: a digital-to-analog converter (DAC, Keithley Instruments, Inc., Solon, OH, part DAC-02), an analog-to-digital converter (ADC, Keithley Instruments, Inc., part KPCI-3108), and a high-precision digital voltmeter (DVM, Keithley Instruments, Inc., part 2000 Multimeter with 20 channel multiplexer).

**Control Systems.** Control functions relied on the DAC channels. Two of the three DAC channels set the output currents used to heat the preheater and reactor. A 0–1 V signal controlled the output current from 0 to 15 A, as needed, with typical currents from 2 to 5 A. The power supplies (Kepco, Inc., Flushing, NY, part ATE 36–15M) acted as high-current operational amplifiers that establish a constant current for a given input setting. Current stability was seen to be excellent: 1 mA in 10 A (10 ppm) over several-hour periods.

For successful external control of both power supplies, the positive terminals must be used as the common connection, because the Kepco supply uses the positive terminal as an analogue common for its control output. If the negative terminals are connected, current set points on one unit interact with the other, making independent adjustments impossible. It is also

(6) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics*, **1996**, *15*, 1518–1520.

(7) Chromatography Sourcebook, Catalogue 500; Alltech Associates, Inc.: Deerfield, IL, 2000–2001; p 531.

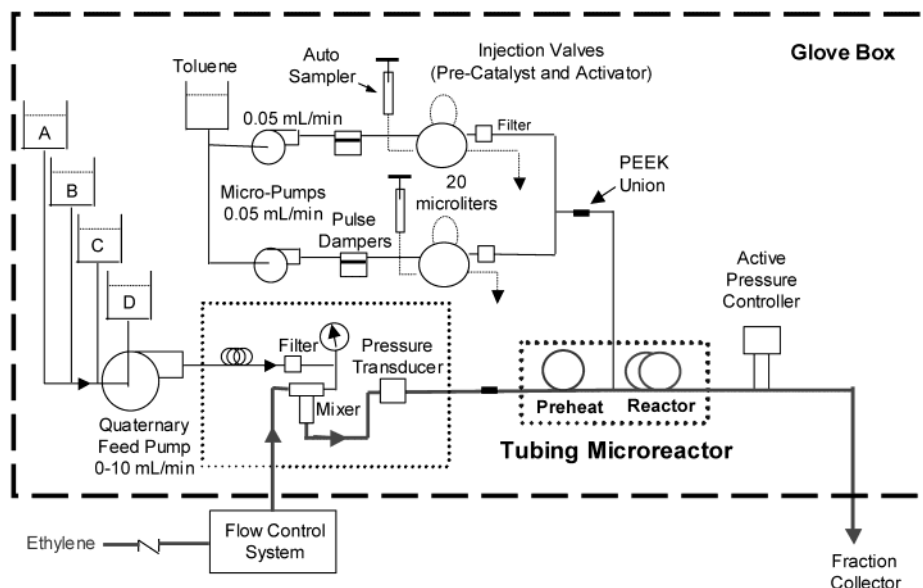


Figure 3. Electrothermal microreactor (ETMR) as configured for ethylene polymerization. The glovebox affords a subparts-per-million oxygen environment to protect the catalysts. The arrangement of Figure 2 is highlighted in the lower right of this figure. Note the PEEK unions installed to provide electrical isolation.

advisable to place the current shunts in the negative polarity legs to reduce further any interactions between current set points.

Initially, temperatures were manually adjusted with trial-and-error settings of the power supply currents. More recently, the software was modified to permit automated, independent temperature control of the preheater and reactor on the basis of temperatures sensed using the voltage tap array method and proportional integral derivative (PID) feedback control. An added feature locks out PID control during the reaction responses, allowing them to be observed as unaltered excursions from the set point temperature value.

**Temperature Measurement and Data Input.** As mentioned above, temperatures are calculated from tubing resistance. Voltage and current measurements are made to obtain resistance, voltage divided by current. A "four-wire" method must be used to obtain reliable results, strictly separating the current-carrying path from the voltage-measurement paths. The objective is to measure only voltage drops associated with the tubing and to avoid those associated with the wires that supply excitation current or junctions of these wires with the tubing. Current is monitored by the voltage developed across a 0.01 ohm current shunt.

Two independent data input paths were used, an analog-to-digital converter (ADC) and a Keithley multiplexing digital voltmeter (DVM). This permits two modes of operation: a standby mode used to reach operating conditions and a run mode for data logging of very precise readings. In standby mode, the ADC/computer monitors and controls preheat temperature, reactor temperature, pressure, and ethylene mass flow, with full system updates obtained at a rate of 10 Hz. In run mode, the DVM/computer monitors, at 0.6 Hz, temperatures of all seven zones of the reactor as well as system pressure. Reactor and preheat temperatures are controlled either by manual adjustments to heating currents or by computer PID loops that use temperatures calculated from zone 7 of the reactor and the preheater, respectively. Run data and instrument settings are stored to disk for future reference or analysis.

Temperature measurement requires a high degree of precision for ascertaining both voltage and current, since a 1 °C temperature rise corresponds to a resistance increase of only 0.08% or 800 ppm. The DVM was chosen over the ADC because of its superior resolution (22 vs 16 bit) and its greater immunity to noise pickup. Given this system design, temperature resolution for the ETMR has been shown to be 0.01 to 0.05 °C from a statistical analysis of baseline noise.

**Pressure Control Electronics.** An important issue that arose during initial testing of the system was widely varying reactor pressures when polymer was formed. This was a consequence of the higher viscosity of the pulses of polymer encountering the small passages of the system. It was clear that some form of pressure management device capable of flow cell temperatures up to 140 °C was needed to allow control of reactor pressure despite the formation of higher viscosity polymer. Commercial units such as the Proportion-Air servo controller valve (Proportion-Air, Inc., McCordsville, IN, part BB2MF-EE500) were investigated but perceived to be inappropriate for this application because of their limited response characteristics, large flow-through volumes relative to the scale of the ETMR, or limited temperature rating. Therefore, the device shown in Figure 4 was created.

A pressure transducer (Validyne Engineering Corp., Northridge, CA, part P55D 4-V-1-60-S-4-B), located at the reactor inlet, measures the pressure difference between the reactor inlet and the atmosphere. The inlet pressure is the sum of the pressure drops across the reactor tubing and the pressure controller. The control objective is to maintain a nearly constant pressure at the reactor inlet by changing the pressure drop across the control valve. The control loop causes a solenoid actuator (Trombetta Corp., Menomonee Falls, WI, part Q517, push-type solenoid) to open a diaphragm-type orifice to correct for the transient increased back-pressure along the reactor. A PID controller operating at 10 Hz (Omron Electronics LLC, Schaumburg, IL, part E5AK) was used initially to manage the operation of this subsystem. Improvements in pressure baseline stability are obtained by operating at

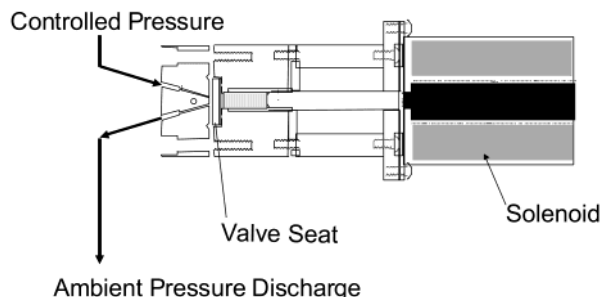


Figure 4. Device for controlling reactor pressures,  $0.35\text{--}6.9 \pm 0.007$  MPa ( $50\text{--}1000 \pm 1$  psig), with a  $50\text{-}\mu\text{L}$  flow volume. The solenoid controls the force acting on the perfluoroalkoxy (PFA) Teflon diaphragm at the valve seat in order to oppose flow in a variable way and, thus, control upstream pressure. The unit easily tolerates operating temperatures up to  $140^\circ\text{C}$ . Figure 5 shows its control capabilities during viscosity fluctuations.

increased control loop frequencies: 100 Hz with TestPoint software on a PC and 8 kHz with a digital signal processor (Texas Instruments, Inc., Houston, TX, part TMDS3200031).

The pressure transducer outputs a 0–5 VDC signal proportional to its full-scale span of 8.6 MPa (1250 psi), providing an input for the controller. The output signal from the PID controller is resistively divided and fed to the power supply (Kepco, Inc., part ATE 36-3M) used to drive the solenoid actuator. The voltage divider ratio is set such that full-scale output from the PID controller gives  $\sim 3$  amp solenoid current. Nominal solenoid ratings are 24 VDC, a maximum sustained power dissipation of 65 W, a force in the range of 200 Newtons, and a response time of 0.3 s to reach rated force at 24 VDC.

Tests to evaluate the effect of pressure controller temperature, and hence, eluent viscosity, were carried out, with the satisfactory observation that the pressure remained stable as temperatures ranged from  $120^\circ$  to  $190^\circ\text{C}$ . The valve's flow-through volume is  $\sim 50\text{ }\mu\text{L}$ .

## RESULTS AND DISCUSSION

Prior to the work with ethylene, the first phase tests looked at the thermally activated decomposition of di-*tert*-butyl peroxide in toluene, a simpler, single-stream test not requiring the mixing of reactants. The results showed that the technique is highly sensitive and reproducible. The next phase of development used the tubing microreactor to polymerize styrene monomer with and without injected initiator. This version of the system successfully formed polystyrene within the toluene carrier, increasing the viscosity of the reactor effluent, as expected.

On the basis of the reasonable system performance using peroxide and then styrene reactants, the next stage of development of the ETMR turned to the far more difficult challenge of reacting ethylene to form polyethylene. This required (1) containing the entire flow system within an oxygen-free ( $<1$  ppm, v/v) drybox; (2) using a quaternary feed pump for introducing various comonomer additives; (3) creating a system to blend ethylene gas into solvent reliably; (4) employing specialized low-flow, controllable pumps to feed separate streams of catalyst and cocatalyst formulations to the reaction zone in the microliter/min flowrate range; (5) providing an electro thermal preheat zone to bring reactant monomer up to reactor temperature prior to catalyst

Table 1. Typical Run Parameters

solvent	toluene
total solvent flow rate	2.0 mL/min
concn of CGC precatalyst	0.020 M
concn of activator	0.020 M
volume of injection loops (each)	20 $\mu\text{L}$
catalyst stream feed rate (each pump)	50 $\mu\text{L}/\text{min}$
ethylene addition rate (gas phase)	25.0 std. mL/min
pressure	2.8 MPa (400 psig)
temperature	$175^\circ\text{C}$

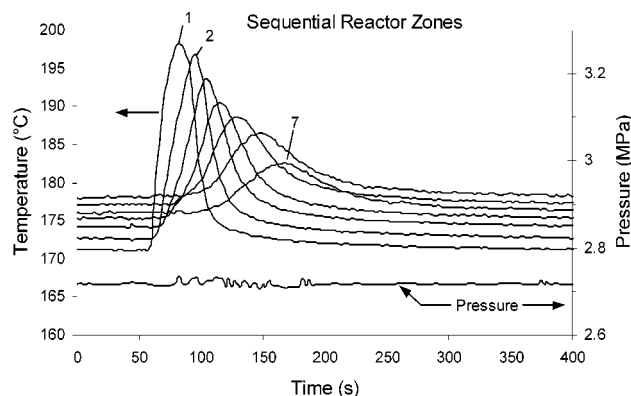


Figure 5. Typical results from an ethylene polymerization run showing simultaneous plots of all seven "zone" temperatures in response to catalyst injection. Peak spreading is a consequence of both axial heat transfer and mixing of the injected zone of catalyst within eluent. The bottom trace shows concurrent reactor pressure, with the control valve system operating at 100 Hz. Increasing the control loop speed to 8 kHz improves pressure control to the point that these variations during polymerizations become indistinguishable from the baseline.

addition; (6) furnishing an autosampler to sequence a variety of catalyst injections for testing quickly; (7) installing an array sample collector to gather effluent polymer product aliquots for subsequent analysis; and (8) developing a user interface in TestPoint running within an IBM PC to manage all these system components while gathering, displaying and storing data. Typical run parameters for the ETMR ethylene polymerizing reactions are listed in Table 1.

An example of the information elicited from a reaction in the system is shown in Figure 5. Assuming 16-cm lengths of 1.27-mm (0.050 in.) i.d. tubing, the zones represent consecutive reactor segments of  $\sim 200\text{ }\mu\text{L}$  each. In this example, the zone temperature patterns are decreasing in maximum temperatures, progressing through the zones from 1 to 7. The lower trace shows the concurrent reactor pressure, as measured in the flow-through pressure transducer shown previously in Figure 3.

At these dimensions and typical 2 mL/min range flow rates, Reynolds numbers are well below the regime of turbulence. So under laminar flow conditions with generally Newtonian solutions, the parabolic distribution of velocities with maximum flow at the tube axis leads to spreading of the injected zone in a fashion typical of LC.<sup>8,9</sup> Thus, we attribute the broadening of the temperature peaks seen in a typical ETMR output pattern to a broadening of

(8) Giddings, J. C. *Chromatography*, 3rd ed.; Van Nostrand: New York, 1975; Chapter 3.

(9) Ruzicka, J.; Hansen, E. H. *Flow Injection Analysis*, John Wiley & Sons: New York, 1981; Chapter 2.



Table 2. Microreactor Reproducibility with Active Pressure Control Using Run Parameters Listed Below

run no.	data file	Output Response: Peak Area ( $\Delta$ °C • s)							total
		zone 1	zone 2	zone 3	zone 4	zone 5	zone 6	zone 7	
1	060500_n06.dat	1516.7	1414.5	1075.2	789.6	510.1	251.2	154.5	5711.8
2	060500_n07.dat	1519.9	1420.1	1083.3	805.5	507.6	256.5	135.1	5728.0
3	060600_n00.dat	1502.6	1390.8	1063.6	790.1	501.7	223.0	134.9	5606.7
4	060600_n01.dat	1446.2	1430.6	1101.1	823.2	525.3	257.2	146.5	5730.0
5	060600_n02.dat	1464.2	1474.1	1132.6	845.8	558.4	266.4	140.2	5881.7
6	060607_n00.dat	1450.3	1423.1	1128.6	858.7	561.3	274.2	142.6	5838.8
7	060607_n02.dat	1428.8	1426.5	1122.0	844.6	551.1	277.8	114.4	5765.2
mean response		1475.5	1425.7	1100.9	822.5	530.8	258.0	138.3	5751.7
SD		37	25	28	28	26	118	13	90
% RSD		2.5	1.8	2.5	3.4	4.8	7.1	9.1	1.6

Run parameters: 2.0 mL/min solvent flow, 25 std mL/min ethylene (gas), 0.020 M concentrations for precatalyst (CGC-cyclopentadienyl) and activator, 20- $\mu$ L injector loops.

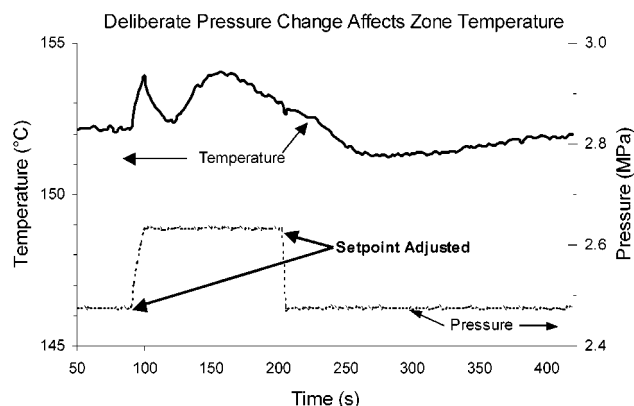


Figure 6. Sensitivity of the ETMR to a sudden change in pressure using deliberate set point adjustments. The temperature response relates to the variation in flow induced by the pressure change. This shows the rapid speed of response of the pressure controller and illustrates that pressure control is essential for maintaining temperature baseline stability.

the mixing zone as the catalyst plug proceeds through the reactor together with heat transfer effects. It is important to recognize that, unlike chromatography where concentrations are detected, the observed responses are purely thermal in nature.

Control of reactor pressure is essential for maintaining stable temperature baselines. Pressure control was engaged to give the results of the type shown in Figure 5. Pressure stability has been improved, as compared to that of Figure 5, by increasing the speed of the PID control loop, as discussed in the figure caption.

Sensitivity of baseline temperature to a deliberate change in back-pressure is seen in Figure 6. This resembles the type of pressure change caused by increased solution viscosity as ethylene polymerizes to polyethylene within the reactor. The pressure rise causes a transient flow decrease that results in temporary overheating due to the reduced thermal load. The presence of a compressible gas–liquid interface at the ethylene saturator adds to this effect in this particular flow configuration. These observations underscore the value of the specialized pressure control device created for the ETMR system.

**Determination of Peak Areas.** Table 2 summarizes the tubing reactor's performance. A high degree of reproducibility is seen despite the fact that these samples were run over a span of 3 days, as recorded in the prefix of the data file name. The relative

standard deviation (%RSD) for total peak area is 1.6%. In general, typical relative standard deviations for total peak areas are 2–5% with active pressure control. Therefore, it is possible to compare and resolve quite subtle trends in chemical reactivities and process conditions.

For the sake of discussion, from this point forward data will be shown as output responses obtained by integrating each of the seven zone temperature pulses from a given catalyst injection and then adding them together to give total area, which is a measure of heat released. This affords a standard way to compare responses. It's also important to note that system precisions listed in Table 2 are best for the total of the zones taken together rather than zone by zone. The explanation is that there may be variations in the location of the reaction maximum from run to run, affecting a given zone's reproducibility, whereas the total output from the overall reaction is quite reproducible by comparison.

The following experiment was performed to correlate output response with the amount or weight of polymer produced. Ethylene flow rate was varied from 3.0 to 50.0 std mL/min while total responses were recorded. Corresponding polymer weights were obtained after stripping toluene solvent from samples collected with the fraction collector. A linear correlation was obtained for total response area versus sample weight, with the correlation line intercepting the origin and displaying a slope of 249 ( $\Delta$  °C) s/mg polyethylene ( $R^2 = 0.993$ ). This implies that total response area can be used satisfactorily as an indication of the amount of polyethylene produced.

Figure 7 shows a comparison of relative activities for two different catalysts under the same reaction conditions. Each plotted point is the average of three runs with error bars showing a range of plus and minus one standard deviation. In some cases, the error bars are smaller than the size of the plotting symbol itself. The results in the figure reveal that the "constrained geometry catalyst," CGC-cyclopentadienyl, is  $\sim 3.6$  times as reactive at 0.005 M feed and is 1.5 times as reactive at 0.020 M feed. Actual catalyst concentrations in the reactor are reduced about 20-fold, because the catalyst stream is diluted by the flow rate ratio at the mixing tee when it is introduced into the reactor.

Figure 8 compares catalyst activity for the same catalyst (CGC-cyclopentadienyl) at two different temperatures. As before, plotted points are each the average of three runs. It can be observed that catalyst activity is greater at the lower temperature, 155 °C. A

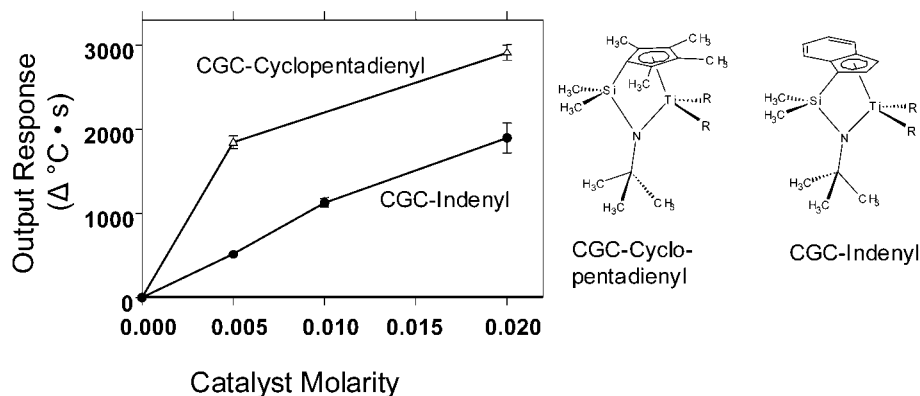


Figure 7. Comparison of results for ethylene polymerizations using two different catalysts at 155 °C. The output responses are determined from the combined temperature pulse time integrals. A LEAP Technologies auto injector allows unattended multiple catalyst and associated activator injections within the glovebox environment, generating data on reproducibility. Catalysts of different structures clearly differ in reactivity at equivalent concentrations.

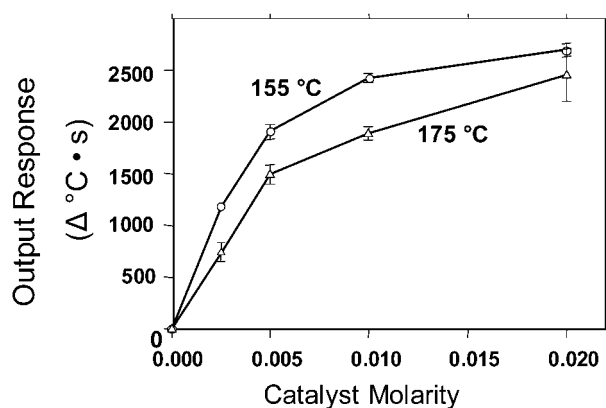


Figure 8. Effect of run temperature on ethylene polymerizations using CGC-cyclopentadienyl catalyst. Temperature sensitivities of catalysts are of critical concern, since they determine the operating conditions of production processes. All of the experiments generating these data required a total of only 4 mg of CGC-cyclopentadienyl component prior to adding activator that generates the active catalyst. Use of the ETMR offers an advantage when only small amounts of a new catalyst are available for evaluation.

likely explanation is that this catalyst degrades more rapidly at higher temperatures.

The findings illustrated in Figures 7 and 8 are in agreement with polymerization runs made in standard 2.0 L Parr reactors. Only ~4–6 runs/day are possible with a single Parr reactor. In contrast, ~10 runs/hour are possible with the ETMR. Rapid analysis and high precision make it possible to explore subtle

trends among various catalysts and reaction conditions. Alternating among control and unknown samples increases confidence in these observations.

## CONCLUSIONS

Although requiring only minimal amounts of reactants and catalyst formulations, the electrothermal microreactor (ETMR) can provide a rich amount of information regarding chemical reactions. It offers the ability to control reactor temperature and pressure over a wide range while managing the addition of reactants under changing conditions. Treating the tubing wall itself like a temperature sensor array affords direct insight into the reaction activities, particularly since measured responses are seen to be proportional to the amount of polymer produced. The speed, accuracy, scale and flexibility of this new approach are prompting further applications in the realm of high-throughput studies of chemical reactions.

## ACKNOWLEDGMENT

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